

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 695 812 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.02.1996 Bulletin 1996/06

(51) Int. Cl.⁶: **C22C 45/02**, H01F 1/153,
H01F 3/04

(21) Application number: **95111776.1**

(22) Date of filing: **26.07.1995**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **01.08.1994 JP 180037/94**

(71) Applicant: **HITACHI METALS, LTD.**
Chiyoda-ku, Tokyo (JP)

(72) Inventor: **Yoshizawa, Yoshihito**
Fukaya-shi, Saitama-ken (JP)

(74) Representative: **Strehl Schübel-Hopf Groening & Partner**
D-80538 München (DE)

(54) **Nanocrystalline alloy with insulating coating, magnetic core made thereof, and process for forming insulating coating on a nanocrystalline alloy**

(57) A nanocrystalline alloy having an insulating coating on at least one of its surfaces is disclosed. The insulating coating is formed from a solution containing at least one insulating material selected from aluminium silicates, lithium silicates and magnesium oxide. By using such a solution, cracking and exfoliation of the insulating coating during the heat treatment for crystallisation of an amorphous alloy can be effectively prevented. Also, an increase in internal stress of the nanocrystalline alloy during the heat treatment can be prevented. Therefore, a nanocrystalline alloy having good insulating properties and magnetic properties suitable for a magnetic core, in particular for a high-frequency magnetic core, can be obtained.

EP 0 695 812 A1

Description

BACKGROUND OF THE INVENTION

5 The present invention relates to nanocrystalline alloy having an insulating coating thereon, which is excellent in high-frequency characteristics and suitable for use in various magnetic parts such as transformer, choke coil, etc., and further relates to a magnetic core made of the nanocrystalline alloy and a method for forming the insulating coating on the nanocrystalline alloy.

10 A nanocrystalline alloy, which contains fine crystal grains having an average grain size of 50 nm or less in an area ratio of 50% or more of the alloy structure, has been, because of its good soft magnetic properties, used for producing magnetic cores of a common-mode choke coil, a high-frequency transformer, an electrical leak alarm, pulse transformer, etc. Typical examples for such a nanocrystalline alloy are disclosed in U.S. Patent No. 4,881,989 and JP-A-1-242755. The nanocrystalline alloy known in the art has been generally produced by subjecting an amorphous alloy obtained by quenching a molten or vaporized alloy to a heat treatment for forming fine crystals. A method for quenching a molten alloy to produce an amorphous alloy may include a single roll method, a twin roll method, a centrifugal quenching method, 15 a rotation spinning method, an atomization method, a cavitation method, etc. A method for quenching a vaporized metal may include a sputtering method, a vapor deposition method, an ion plating method, etc. The nanocrystalline alloy is produced by finely crystallizing an amorphous alloy produced by the above method, and is known to have, contrary to amorphous alloys, a good heat stability as well as a high saturation magnetic flux density, a low magnetostriction, and 20 a good soft magnetic property. The nanocrystalline alloy is also known to show a little change with time in its properties and have a good temperature stability.

Conventionally, the magnetic core used in a noise filter, a pulse transformer, etc. has been made of a highly permeable material having good high-frequency characteristics such as ferrite, an amorphous alloy, etc. In a high-frequency transformer for an inverter, a material low in the magnetic core loss has been used. Further, the Fe-based nanocrystalline alloy disclosed in U.S. Patent No. 4,881,989 is described to have a high permeability and a low magnetic core loss, and 25 therefore, suitable for the use mentioned above.

However, it has been found by the inventor that a magnetic core for a common-mode choke coil or a high-frequency magnetic core for an inverter transformer made of thin ribbon of an Fe-based nanocrystalline alloy does not exhibit sufficient properties when the surface of the thin ribbon is not smooth and the thin ribbons are not subjected to layer 30 insulation because the influence of eddy current on the properties comes to remarkable with increasing width of the thin ribbon. As a method of layer insulation, JP-A-63-302504 discloses to apply SiO₂ powder or MgO powder on a part of or complete surface of a thin alloy ribbon or to coat a thin alloy ribbon with an alcohol solution of a modified alkyl silicate added with an acid. JP-A-2-297903 discloses to form a heat-resistant insulating layer of 0.5-5 μm thick by heating a coating comprising a uniform mixture of 20-90 weight % (calculated in terms of SiO₂) of a silanol oligomer and 80-10 35 weight % of a ceramic fine particle to allow the oligomers cross-linked each other.

However, since an amorphous alloy contracts during the heat treatment for nanocrystallization, an insulating layer on the alloy is cracked or separated from the surface of the alloy due to the contraction stress. Also, sufficient magnetic properties cannot be attained due to the internal stress of the alloy generated by contraction. Although the method disclosed in JP-A-2-297903 solved these problems, the insulating layer formed by the method has a poor affinity for a 40 resin. Therefore, when a magnetic core, for example, for an inverter transformer made of a thin alloy ribbon having such an insulating layer is cut after impregnation with a resin, the resin exfoliates from the cut surface and the thin alloy ribbons are not laminated each other. In the method wherein SiO₂ powder or MgO powder is applied on the surface of an alloy, the powder is likely to be separated from the alloy surface during the production of the magnetic core to lead to insufficient insulation.

45 The influence of the contraction by the heat treatment is not necessary to be considered when an amorphous alloy provided with an insulating coating is produced. However, as described above, the contraction during the heat treatment causes defective insulation due to cracking or peeling of the insulating coating or deterioration of magnetic properties due to increased internal stress. Therefore, an insulating coating free from the above problems and a method for forming such an insulating coating on a nanocrystalline alloy has been demanded to be developed. Further, an insulating coating 50 exhibiting sufficient insulation properties even if the insulating coating is made thinner has been required in the field of electronic circuitry which requires a small-sized magnetic core.

OBJECT AND SUMMARY OF THE INVENTION

55 Accordingly, an object of the present invention is to provide a nanocrystalline alloy excellent in insulating properties. Another object of the present invention is to provide a magnetic core excellent in magnetic properties at high frequency, and still another object of the present invention is to provide a method for forming an insulating coating free from the conventional problems.

As a result of the intense research in view of the above objects, the inventor have found that an insulating coating formed by heating a solution of at least one insulating material selected from the group consisting of aluminum silicates, lithium silicates and magnesium methylate is free from cracking and peeling during the heat treatment for crystallization of an amorphous alloy, and a nanocrystalline alloy provided with such an insulating coating is excellent in insulating properties and suitable as a material for magnetic core used at high frequency. The present invention has been accomplished based on the finding.

Thus, in a first aspect of the present invention, there is provided a nanocrystalline alloy having on at least one surface thereof an insulating coating, the nanocrystalline alloy having a chemical composition represented by the following formula:



wherein M is at least one element selected from the group consisting of Co and Ni, A is at least one element selected from the group consisting of Cu and Au, M' is at least one element selected from the group consisting of Ti, V, Zr, Nb, Mo, Hf, Ta and W, M'' is at least one element selected from the group consisting of Cr, Mn, Al, Sn, Zn, Ag, In, platinum group elements, Mg, Ca, Sr, Y, rare earth elements, N, O and S, X is at least one element selected from the group consisting of B, Si, C, Ge, Ga and P, and each of a, x, y, z and b respectively satisfies $0 \leq a \leq 0.5$, $0 \leq x \leq 10$, $0.1 \leq y \leq 20$, $0 \leq z \leq 20$ and $2 \leq b \leq 30$, and the insulating coating having an average thickness of 2 μm or less and comprising at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium oxide.

In a second aspect of the present invention, there is provided a magnetic core made of the nanocrystalline alloy as defined above.

In a third aspect of the present invention, there is provided a method for forming an insulating coating on a nanocrystalline alloy, which comprises (1) rapidly quenching a molten alloy having a chemical composition represented by the following formula:



wherein M is at least one element selected from the group consisting of Co and Ni, A is at least one element selected from the group consisting of Cu and Au, M' is at least one element selected from the group consisting of Ti, V, Zr, Nb, Mo, Hf, Ta and W, M'' is at least one element selected from the group consisting of Cr, Mn, Al, Sn, Zn, Ag, In, platinum group elements, Mg, Ca, Sr, Y, rare earth elements, N, O and S, X is at least one element selected from the group consisting of B, Si, C, Ge, Ga and P, and each of a, x, y, z and b respectively satisfies $0 \leq a \leq 0.5$, $0 \leq x \leq 10$, $0.1 \leq y \leq 20$, $0 \leq z \leq 20$ and $2 \leq b \leq 30$ to produce an amorphous alloy; (2) coating on at least one surface of the amorphous alloy a solution containing at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium methylate; (3) drying the solution-coated amorphous alloy at a temperature between 80°C and 350°C; and (4) heat-treating the dried amorphous alloy at a temperature not lower than a crystallization temperature of said amorphous alloy so as to form a fine crystal grain having a grain size of 30 nm or less in alloy structure while forming said insulating coating having a thickness of 2 μm or less and comprising at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation illustrative of one embodiment of the method of the present invention;

Fig. 2 is a schematic representation illustrative of another embodiment of the method of the present invention;

Fig. 3 is a schematic representation illustrative of still another embodiment of the method of the present invention; and

Fig. 4 is a schematic view showing a toroidal magnetic core of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The nanocrystalline alloy of the present invention which has an insulating coating on at least one surface thereof may be produced as described below.

First, an amorphous alloy is produced by rapidly quenching a molten alloy having a chemical composition represented by the following formula:



wherein M is at least one element selected from the group consisting of Co and Ni, A is at least one element selected from the group consisting of Cu and Au, M' is at least one element selected from the group consisting of Ti, V, Zr, Nb, Mo, Hf, Ta and W, M'' is at least one element selected from the group consisting of Cr, Mn, Al, Sn, Zn, Ag, In, platinum group elements, Mg, Ca, Sr, Y, rare earth elements, N, O and S, X is at least one element selected from the group consisting of B, Si, C, Ge, Ga and P, and each of a, x, y, z and b respectively satisfies $0 \leq a \leq 0.5$, $0 \leq x \leq 10$, $0.1 \leq y \leq 20$, $0 \leq z \leq 20$ and $2 \leq b \leq 30$. A single-roll method, a twin-roll method, etc. may be employed to rapidly quenching the molten alloy.

A chemical composition outside the above range fails to give a sufficient effect attained by the present invention due to a remarkable reduction in specific permeability or a remarkable increasing in magnetic core loss, thereby making it unable to obtain a nanocrystalline alloy of practical characteristics.

Then, a solution of at least one insulating material is applied on at least one surface of the amorphous alloy thus produced. The insulating material is selected from the group consisting of aluminum silicates, modified aluminum silicates, lithium silicates and magnesium methylate. The solution may include oxide powder, nitride powder, etc. which is known to be used for insulating coating. The concentration of the insulating material in the solution is preferably 5 to 50 % by weight. The solution thus prepared may be mixed with a solution of colloidal silica. The solution may be applied on an amorphous alloy after subjecting the amorphous alloy to anodizing treatment which improves the insulating properties and corrosion resistance of the resulting nanocrystalline alloy. The amount of the solution being applied on the amorphous alloy is regulated so that the thickness of the resulting insulating coating may be 2 μm or less.

The amorphous alloy applied with the solution is then dried at a temperature of 80-350°C, preferably for 5 seconds to 10 minutes. The drying may be effected by blowing the applied solution with air or another gas such as argon, nitrogen, helium, etc. maintained at 80-350°C to rapidly dry the solution. This makes the insulating coating uniform in its thickness.

Before subjected to the subsequent heat treatment, the amorphous alloy thus dried is usually made into a form of magnetic core by winding the thin ribbon of amorphous alloy or laminating cut sheets or punched sheets of the amorphous alloy. The winding or laminating step may be carried out after heat treatment when the heat-treated alloy ribbon is sufficiently flexible.

The heat treatment for crystallization is carried out at a temperature not lower than the crystallization temperature of the amorphous alloy, usually at 450-700°C, for 1 minute to 24 hours in an inert gas atmosphere such as nitrogen gas atmosphere, argon gas atmosphere, etc. or an oxidizing atmosphere such as air. By this heat treatment, fine crystal grains are formed in the alloy structure, and simultaneously, the insulating coating is formed on the surface of the resulting nanocrystalline alloy. During the heat treatment, the magnesium methylate is oxidized to provide an insulating coating comprising magnesium oxide.

When an amorphous alloy applied with the solution is directly subjected to heat treatment without being dried, the heat-treatment atmosphere comes to contain a large amount of moisture evaporated from the solution. This leads to a preferential crystallization of the surface of the alloy. As a result, a nanocrystalline alloy of a uniform and fine structure cannot be obtained. Also, cracking and peeling of the insulating coating are likely to occur. Therefore, the drying step prior to the heat treatment of crystallization is indispensable.

The production method of the present invention will be further described while referring to the drawings.

In Fig. 1, a thin ribbon 1 of amorphous alloy, which is unwound in the direction indicated by the arrow from a winding reel 2, is allowed to pass through a solution 4 stored in a vessel 3 to apply the solution 4 on both the surface of the thin ribbon 1 of amorphous alloy. After passing through a scraper 5, the thin ribbon 1 of amorphous alloy is introduced into a drying furnace 6 kept at 80-350°C. The dried thin ribbon 1 of amorphous alloy is then wound on a winding reel 7 and subjected to the subsequent heat treatment of crystallization.

In Fig. 2, a thin ribbon 1 of amorphous alloy, which is unwound in the direction indicated by the arrow from a winding reel 2, is allowed to pass through a roll coater 8. A transfer roll 10 is partially immersed in a solution 4 stored in a vessel 3 to apply the solution 4 on the lower surface of the thin ribbon 1 of amorphous alloy, which is then introduced into a

drying furnace 6 kept at 80 - 350°C. The dried thin ribbon 1 of amorphous alloy is then wound on a winding reel 7 and subjected to the subsequent heat treatment of crystallization.

In Fig. 3, the upper surface of a thin ribbon 1 of amorphous alloy, which is unwound in the direction indicated by the arrow from a winding reel 2, is sprayed with a solution 4 from a spray 9. The thin ribbon 1 of amorphous alloy is then introduced into a drying furnace 6 kept at 80-350°C. The dried thin ribbon 1 of amorphous alloy is then wound on a winding reel 7 and subjected to the subsequent heat treatment of crystallization.

The nanocrystalline alloy produced by the method described above has preferably a thickness of 2 to 50 μm and contains fine crystals having an average grain size of 30 nm or less, preferably in an area ratio of 50 % or more. The fine crystals mainly comprise bcc Fe-phase (body centered cubic lattice phase) containing Si, and may contain an ordered lattice phase or are constituted of ordered lattice. Alloying elements other than Si, i.e., B, Al, Ge, Zr, etc. may be contained as a solid solution component in the bcc Fe-phase. The remaining part other than the crystal phase mainly comprises amorphous phase. However, a nanocrystalline alloy substantially comprising only crystal phase is also embraced within the scope of the present invention. A compound phase may also be formed in a part of the alloy structure.

The average thickness of the insulating coating is 2 μm or less, preferably 0.01 to 1 μm . An average thickness of 0.5 μm or less is particularly preferred because the size of magnetic core can be reduced while maintaining its excellent insulating properties.

A solution of aluminum silicate ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) provides the surface of nanocrystalline alloy with an insulating coating having a uniform thickness and a high resistance to peeling because internal stress is hardly generated in the alloy during the crystallization process. Therefore, the insulating properties can be improved. A nanocrystalline alloy having such an insulating coating exhibits a high permeability and a low magnetic core loss at low and high frequency range.

A solution of lithium silicate ($\text{Li}_2\text{O}\cdot\text{SiO}_2$) produces the same effect as above because internal stress is hardly generated in the alloy during the crystallization process.

Since a solution of magnesium methylate can be dried rapidly, a thin, uniform and hard insulating coating comprising magnesium oxide, which exhibits improved insulating properties, is formed on the nanocrystalline alloy.

The magnetic core made by laminating or winding the nanocrystalline alloy described above is excellent in layer insulation and has little internal stress, and therefore, suitable for magnetic core used in a high-frequency range. In addition, since the nanocrystalline alloy has a good affinity for a resin such as an epoxy-type resin, a cut core having a high interlaminar strength can be obtained.

The present invention will be further described while referring to the following Examples which should be considered to illustrate various preferred embodiments of the present invention.

Example 1

An amorphous alloy ribbon having a width of 25.4 mm and a thickness of 18 μm was produced by quenching a molten alloy of $\text{F}_{\text{bal}}\text{Cu}_{0.9}\text{Nb}_{2.8}\text{Si}_{15.5}\text{B}_{6.2}$ (atomic %) by using a single roll method. After being passed through a solution containing each insulating material listed in Table 1, the amorphous alloy ribbon was dried in a hot-gas furnace kept at 200°C. The dried amorphous alloy ribbon was then wound to form a toroidal shape of 100 mm outer diameter and 80 mm inner diameter, and then heated to 570°C in a furnace at a heating rate of 1 .5°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 12 nm.

For comparison, a toroidal magnetic core having no insulating coating was produced in the same manner as above (Sample No. 9).

The specific permeability (μ_r) at 10 MHz, the magnetic core loss (P_c) at 500 kHz and 0.05 T, the average thickness of the insulating coating and the resistance (R) between the innermost part and the surface of the magnetic core are

shown in Table 1.

Table 1

Sample No.	Insulating Material	μ_r	Pc (kW/m ³)	R (Ω)	Thickness (μm)
Invention					
1	modified aluminum silicate	640	220	135	0.8
2	lithium silicate	650	220	138	0.7
3	magnesium methyllate	590	240	128	0.2
4	lithium silicate	710	210	142	1.2
5	magnesium methyllate	620	260	121	0.1
Comparison					
6	alumina sol	410	360	27	1.1
7	alkyl silicate	490	310	35	1.2
8	colloidal silica	480	330	29	0.2
9	-	120	590	1.1	-

As seen from Table 1, the nanocrystalline alloy having the insulating coating of the present invention had a large value of R, which means a high interlaminar insulating resistance. This results in high magnetic properties of a high μ_r and a low Pc.

Example 2

An amorphous alloy ribbon having a width of 20 mm and a thickness of 18 μm was produced by quenching a molten alloy having each chemical composition shown in Table 2 by using a single roll method. After being passed through a solution dissolving each insulating material listed in Table 2, the amorphous alloy ribbon was dried in a hot-gas furnace kept at 200°C. The dried amorphous alloy ribbon was then wound to form a toroidal shape of 100 mm outer diameter and 80 mm inner diameter, and then heated to 570°C in a furnace at a heating rate of 1 . 5°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 12 nm.

The specific permeability (μ_r) at 10 MHz, the magnetic core loss (Pc) at 500 kHz and 0.05 T, the average thickness of the insulating coating and the resistance (R) between the innermost part the surface of the magnetic core are shown

in Table 2.

Table 2

Sample No.	Composition (atomic %)	Insulating Material
Invention		
10	10 Fe _{bal.} Cu ₁ Hf ₂ Si ₉ B ₁₃	modified aluminum silicate
	11 Fe _{bal.} Cu ₁ Nb ₇ B ₉ Ge ₄	lithium silicate
15	12 Fe _{bal.} Cu ₁ Nb ₃ Y ₁ Si _{16.5} B ₆	magnesium methyllate
	13 Fe _{bal.} Cu _{1.6} Nb ₂ W ₁ Si ₁₆ B ₆ P ₁	lithium silicate
20	14 Fe _{bal.} Au ₁ Nb ₂ Mn ₁ Si ₁₃ B ₇	magnesium methyllate
	15 Fe _{bal.} Cu ₁ Nb ₃ Si ₁₅ B ₇ Ga _{0.001}	lithium silicate
	16 Fe _{bal.} Cu ₁ Mo ₅ Si ₁₆ B ₇ C ₁	magnesium methyllate
25	17 Fe _{bal.} Au ₁ Ti ₁ Nb ₂ Si ₁₄ B ₇ S _{0.001}	lithium silicate
	18 Fe _{bal.} Cu ₁ Nb _{2.5} Si ₁₄ B ₆ Al ₂	modified aluminum silicate
30	19 Fe _{bal.} Ni ₁ Cu ₁ Nb ₃ Si ₁₅ B ₇ N _{0.001}	magnesium methyllate
	20 Fe _{bal.} Co ₁ Cu ₁ Nb ₃ Si ₁₅ B ₇ Sn _{0.06}	lithium silicate
35	21 Fe _{bal.} Cu ₁ Nb ₃ Ru ₁ Si ₁₅ B ₆ In _{0.06}	modified aluminum silicate
	22 Fe _{bal.} Au ₁ Nb ₂ Pd ₁ Si ₁₈ B ₇ S _{0.001}	magnesium methyllate
Comparison		
40	23 Fe _{bal.} Cr ₁ Si ₉ B ₁₃ (amorphous)	alumina sol

2 4 Fe_{bal.}Cr₁Si₉B₁₃ (amorphous) magnesium methyllate

Table 2 (Contd.)

Sample No.	μ_r	Pc (kW/m ³)	R (Ω)	Thickness (μ m)
Invention				
10	610	240	143	2
11	510	290	121	0.2
12	590	300	114	0.1
13	580	260	101	0.1
14	570	270	98	0.05
15	580	260	99	0.09
16	590	250	111	0.12
17	600	220	100	0.1
18	510	390	112	0.15
19	610	210	114	0.14
20	610	210	108	0.15
21	520	370	105	0.14
22	610	210	111	0.12
Comparison				
23	140	650	105	0.12
24	170	600	111	0.12

From Table 2, the magnetic core of the present invention is found to be excellent because of its high permeability (μ_r) and low magnetic core loss (Pc).

Example 3

An amorphous alloy ribbon having a width of 20 mm and a thickness of 12 μm was produced by quenching a molten alloy of $\text{Fe}_{\text{bal}}\text{Cu}_1\text{Nb}_3\text{Si}_{16}\text{B}_{6.5}\text{Cr}_{0.5}\text{Sn}_{0.05}$ (atomic %) by using a single roll method. After being passed through a solution of lithium silicate, the amorphous alloy ribbon was dried in a hot-gas furnace kept at each temperature listed in Table 3. The dried amorphous alloy ribbon having a coating of about 1 μm thick was then wound to form a toroidal shape of 60 mm outer diameter and 50 mm inner diameter, and then heated to 570°C in a furnace at a heating rate of 1.2°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 12 nm.

The specific permeability (μ_r) at 1 kHz of each magnetic core is shown in Table 3.

Further, the brittleness of each nanocrystalline alloy was evaluated by whether brittle fracture occurred when the alloy was bent.

Table 3

Sample No.	Drying Temperature (°C)	μ_r	Brittle Fracture
Invention			
25	80	91200	None
26	100	93200	None
27	150	94500	None
28	200	96800	None
29	250	96700	None
30	300	95800	None
31	350	96100	None
Comparison			
32	40	73200	None
33	60	85900	None
34	380	-	Observed
35	400	-	Observed

When the drying temperature was lower than 80°C (Sample Nos. 32 and 33), the alloy ribbons after heat treatment for crystallization were stuck each other because of insufficient drying to result in reduced magnetic properties. On the other hand, when the dried temperature was higher than 350°C (Sample Nos. 34 and 35), the alloy ribbons were embrittled and easily broken. This made the production of the magnetic core very difficult, and therefore, the permeability (μ_r) was unable to be determined.

Example 4

An amorphous alloy ribbon having a width of 25 mm and a thickness of 12 μm was produced by quenching a molten alloy of $\text{Fe}_{\text{bal}}\text{Nb}_3\text{Ga}_4\text{Si}_{14}\text{B}_7$ (atomic %) by using a single roll method. After being passed through a solution containing each insulating material listed in Table 4, the amorphous alloy ribbon was dried in a hot-gas furnace kept at 200°C. The dried amorphous alloy ribbon was then wound to form a toroidal shape shown in Fig. 4, and then heated to 550°C in a furnace at a heating rate of 1.2°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 14 nm. Each magnetic core was impregnated with an epoxy-type resin and made into a cut core by cutting after the impregnated resin was hardened. The average thickness of the insulating coating, the magnetic core loss (Pc) at 20 kHz and 0.2 T, the resistance (R) between the innermost part and the surface and the

appearance of the cut surface of each magnetic core are shown in Table 4.

Table 4

Sample No.	Insulating Material	Thickness (μm)	Pc (kW/m ³)	R (Ω)	Appearance of cut surface
Invention					
36	aluminum silicate	0.8	42	83	+
37	lithium silicate	0.2	38	95	+
38	magnesium methyllate	0.05	42	81	+
39	lithium silicate	0.1	41	80	+
40	magnesium methyllate	0.1	41	88	+
Comparison					
41	alumina sol	1.2	68	32	-
42	alkyl silicate	1.8	62	41	-
43	-	0	120	0.9	+

Note: "+" means that no exfoliation of the resin and no interlaminar separation were observed at the cut surface, while "-" means that such were observed.

As seen from Table 4, no exfoliation of the resin and no interlaminar separation were observed at the cut surface in the magnetic cores of the present invention, this resulting in a low magnetic core loss. Further, the higher values of R show that the magnetic cores of the present invention are provided with sufficient layer insulation.

Example 5

An amorphous alloy ribbon having a width of 20 mm and a thickness of 15 μm was produced by quenching a molten alloy of Fe_{bal.} Cu₁ Ta₃ Si₁₆ B₆ (atomic %) by using a single roll method. After coating on the surface of the amorphous alloy a solution of each insulating material listed in Table 5 by using a roll coater, the amorphous alloy ribbon was dried in a hot-gas furnace kept at 20 °C. The dried amorphous alloy ribbon was then wound to form a toroidal shape of 35 mm outer diameter and 30 mm inner diameter, and then heated to 550°C in a furnace at a heating rate of 1 . 5°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 12 nm.

The specific permeability (μ_r) at 10 MHz, the magnetic core loss (Pc) at 500 kHz and 0.05 T, the average thickness of the insulating coating and the resistance (R) between the innermost part and the surface of the magnetic core are

shown in Table 5.

Table 5

Sample No.	Insulating Material	μ_r	Pc (kW/m ³)	R (Ω)	Thickness (μm)
Invention					
44	aluminum silicate	640	230	28.0	0.2
45	lithium silicate	650	220	29.1	0.1
46	magnesium methyllate	650	210	29.2	0.01
47	lithium silicate	610	240	27.6	0.05
48	magnesium methyllate	630	220	28.7	0.05
Comparison					
49	alumina sol	380	350	6.2	0.8
50	alkyl silicate	460	320	7.1	1.1

As seen from Table 5, the magnetic cores of the present invention were superior to the comparative magnetic cores because of their high permeabilities, low magnetic core losses and high insulating resistances.

Example 6

An amorphous alloy ribbon having a width of 25 mm and a thickness of 15 μm was produced by quenching a molten alloy of $\text{F}_{\text{bal.}}\text{Cu}_1\text{Zr}_3\text{Si}_{14.5}\text{B}_{6.5}$ (atomic %) by using a single roll method. After spraying on the surface of the amorphous alloy a solution of each insulating material listed in Table 6, the amorphous alloy ribbon was dried in a hot-gas furnace kept at 200°C. The dried amorphous alloy ribbon was then wound to form a toroidal shape of 50 mm outer diameter and 30 mm inner diameter, and then heated to 550°C in a furnace at a heating rate of 1 . 5°C/min and maintained there for 15 minutes to be subjected to heat treatment in a nitrogen atmosphere. The heat-treated product was cooled to room temperature to obtain each magnetic core. The most part of the alloy structure of the resulting nanocrystalline alloy was occupied with extremely fine grains comprising bcc-phase of an average grain size of about 12 nm.

The specific permeability (μ_r) at 10 MHz, the magnetic core loss (Pc) at 500 kHz and 0.05 T, the average thickness of the insulating coating and the resistance (R) between the innermost part and the surface of the magnetic core are shown in Table 6.

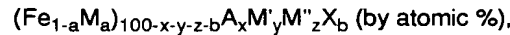
Table 6

Sample No.	Insulating Material	μ_r	Pc (kW/m ³)	R (Ω)	Thickness (μm)
Invention					
51	aluminum silicate	610	240	90.5	0.8
52	lithium silicate	650	220	91.3	0.3
53	magnesium methyllate	640	230	89.5	0.1
54	lithium silicate	560	250	87.6	0.2
55	magnesium methyllate	550	260	86.6	0.06
Comparison					
56	alumina sol	340	360	21.1	1.3
57	alkyl silicate	390	330	23.1	1.1

As seen from Table 6, the magnetic cores of the present invention were superior to the comparative magnetic cores because of their high permeabilities, low magnetic core losses and high insulating resistances.

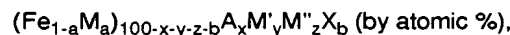
Claims

1. A nanocrystalline alloy having on at least one surface thereof an insulating coating, said nanocrystalline alloy having a chemical composition represented by the following formula:



wherein M is at least one element selected from the group consisting of Co and Ni, A is at least one element selected from the group consisting of Cu and Au, M' is at least one element selected from the group consisting of Ti, V, Zr, Nb, Mo, Hf, Ta and W, M'' is at least one element selected from the group consisting of Cr, Mn, Al, Sn, Zn, Ag, In, platinum group elements, Mg, Ca, Sr, Y, rare earth elements, N, O and S, X is at least one element selected from the group consisting of B, Si, C, Ge, Ga and P, and each of a, x, y, z and b respectively satisfies $0 \leq a \leq 0.5$, $0 \leq x \leq 10$, $0.1 \leq y \leq 20$, $0 \leq z \leq 20$ and $2 \leq b \leq 30$, and said insulating coating having an average thickness of 2 μm or less and comprising at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium oxide.

2. The nanocrystalline alloy according to claim 1, wherein the average thickness of said insulating coating is 0.2 μm or less.
3. A magnetic core produced by laminating or winding said nanocrystalline alloy according to claim 1 or 2.
4. The magnetic core according to claim 3, which is impregnated with an epoxy-type resin.
5. A method for forming an insulating coating on a nanocrystalline alloy, which comprises:
rapidly quenching a molten alloy having a chemical composition represented by the following formula:



wherein M is at least one element selected from the group consisting of Co and Ni, A is at least one element selected from the group consisting of Cu and Au, M' is at least one element selected from the group consisting of Ti, V, Zr, Nb, Mo, Hf, Ta and W, M'' is at least one element selected from the group consisting of Cr, Mn, Al, Sn, Zn, Ag, In, platinum group elements, Mg, Ca, Sr, Y, rare earth elements, N, O and S, X is at least one element selected from the group consisting of B, Si, C, Ge, Ga and P, and each of a, x, y, z and b respectively satisfies $0 \leq a \leq 0.5$, $0 \leq x \leq 10$, $0.1 \leq y \leq 20$, $0 \leq z \leq 20$ and $2 \leq b \leq 30$, to produce an amorphous alloy;

coating on at least one surface of said amorphous alloy a solution containing at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium methyllate;

drying the solution-coated amorphous alloy at a temperature between 80°C and 350°C; and

heat-treating the dried amorphous alloy at a temperature not lower than a crystallization temperature of said amorphous alloy so as to form a fine crystal grain having a grain size of 30 nm or less in alloy structure while forming said insulating coating having a thickness of 2 μm or less and comprising at least one insulating material selected from the group consisting of aluminum silicates, lithium silicate and magnesium oxide.

6. The method according to claim 5, wherein said solution is coated on said amorphous alloy by passing said amorphous alloy through said solution.
7. The method according to claim 5, wherein said solution is coated on said amorphous alloy by passing said amorphous alloy through a roll coater.
8. The method according to claim 5, wherein said solution is coated on said amorphous alloy by spraying said solution on the surface of said amorphous alloy.

9. The method according to any one of claims 5 to 8, wherein said amorphous alloy is coated with said solution after the surface of said amorphous alloy is subjected to anodizing treatment.
- 5 10. The method according to any one of claims 5 to 9, wherein said amorphous alloy coated with said solution is dried by blowing a hot air, argon gas, nitrogen gas or helium gas onto the surface of said amorphous alloy.

10

15

20

25

30

35

40

45

50

55

FIG. 1

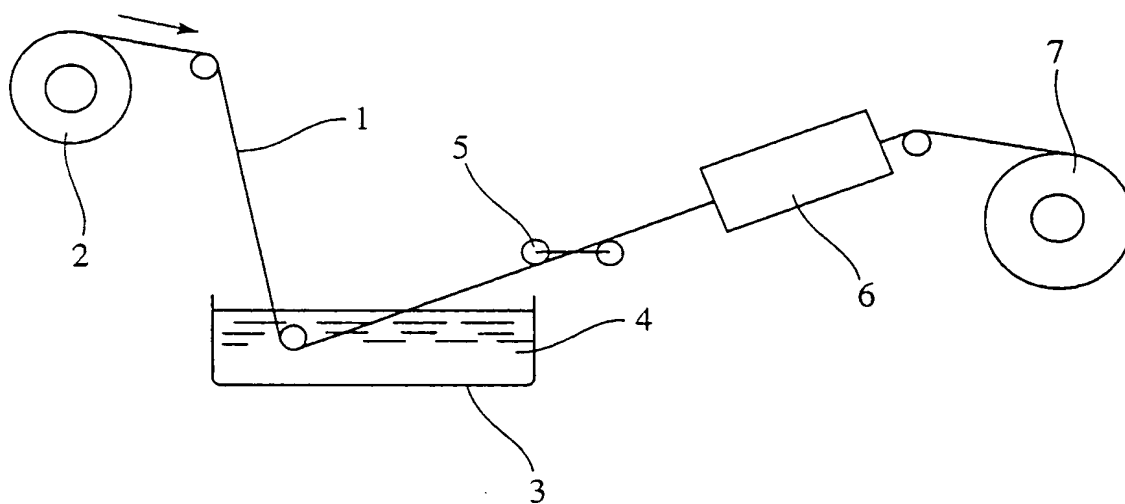


FIG. 2

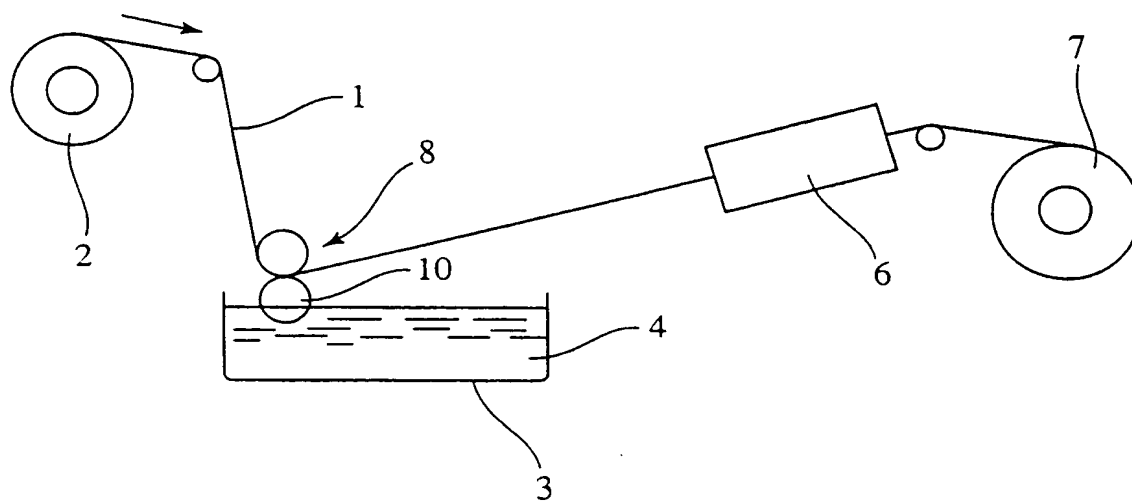


FIG. 3

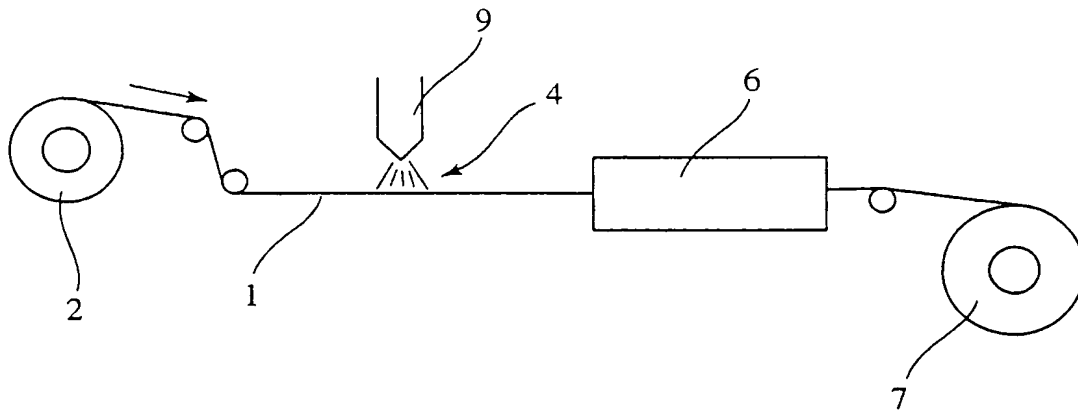
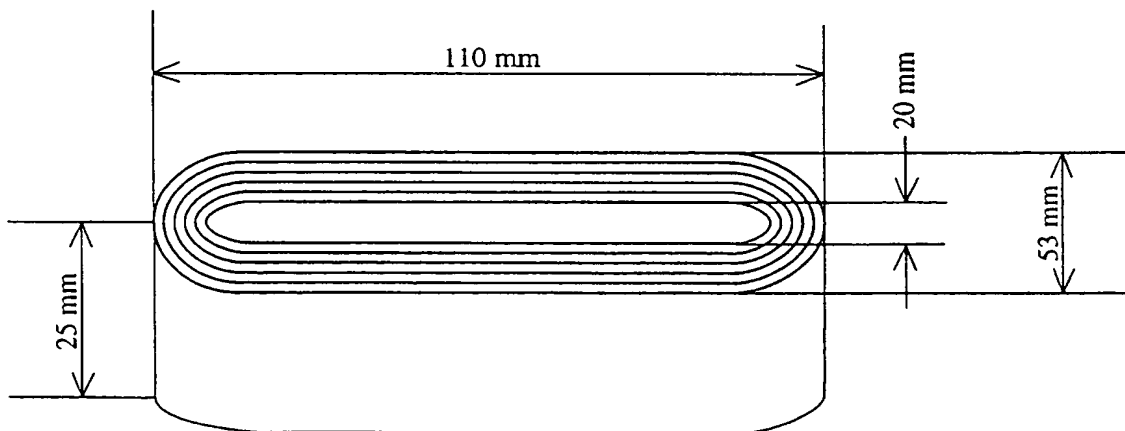


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 1776

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-5 083 366 (ARAKAWA ET AL.) * the whole document *	1,5,6	C22C45/02 H01F1/153 H01F3/04
A,D	& JP-A-2 297 903 (HITACHI) ---	1,5,6	
Y	EP-A-0 400 550 (TDK CORPORATION) *Claims 1-30*	1	
Y	EP-A-0 585 940 (HITACHI METALS) * the whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C22C H01F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 October 1995	Examiner Lippens, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 150 01.82 (P04C01)